Reduction of Low Temperature Engine Pollutants by Understanding the Exhaust Species Interactions in a Diesel Oxidation Catalyst

Lefort, Isaline; Herreros, Jose; Tsolakis, Athanasios

DOI:
10.1021/es4051499

Reduction of Low Temperature Engine Pollutants by Understanding the Exhaust Species Interactions in a Diesel Oxidation Catalyst

I. Lefort, J.M. Herreros, A. Tsolakis*

School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

* Tel.: +44 (0) 121 414 4170, fax: +44 (0) 121 414 7484; a.tsolakis@bham.ac.uk

Abstract

The interactions between exhaust gas species and their effect (promotion or inhibition) on the light-off and activity of a diesel oxidation catalyst (DOC) for the removal of pollutants are studied, using actual engine exhaust gases from the combustion of diesel, alternative fuels (rapeseed methyl ester and gas-to-liquid fuel) and diesel/propane dual fuel combustion. The activity of the catalyst was recorded during a heating temperature ramp where carbon monoxide (CO) and hydrocarbon (HC) light-off curves were obtained. From the catalyst activity tests, it was found that the presence of species including CO, medium-heavy HC, alkenes, alkanes and NO_x and their concentration influence the catalyst ability to reduce CO and total HC emissions before release to the atmosphere. CO could inhibit itself and other species oxidation (e.g. light and medium-heavy hydrocarbons) while suffering from competitive adsorption with NO. Hydrocarbon species were also found to inhibit their own oxidation as well as CO through adsorption competition. On the other hand, NO_2 was found to promote low temperature HC oxidation through its partial reduction, forming NO. The understanding of these exhaust species interactions within the DOC could aid the design of an efficient aftertreatment system for the removal of diesel exhaust pollutants.

Keywords

DOC; CO/HC light-off; alternative fuels; exhaust species interactions

Introduction

Recently, the International Agency for Research on Cancer (IARC) changed the classification of diesel engine exhaust from *possibly carcinogenic to human* (Group 2A) in 1988 to *carcinogenic to human* (Group 1) in 2012 [1]. This classification justifies the ever tightening emission legislations imposed on diesel cars affecting the air pollution. The trend for this legislation is now to focus more on cold start and low to medium load emissions which can be produced in the urban environment when low vehicle speed, stop/start and idle phases are frequent [2]. It is also in these urban environments that humans are more exposed to vehicle exhaust gas. Several strategies have been developed in order to reduce the quantity of pollutants emitted to the atmosphere and among them is the use of the diesel oxidation catalyst (DOC) which oxidises CO and HC to CO_2 and water before release to the atmosphere. Another potential role of the DOC is to oxidise NO to NO_2 for use in passive regeneration of the diesel particulate filter (DPF) downstream of the DOC in the engine exhaust [3] or to enhance NO_x reduction in the selective catalytic reduction (SCR) process [4]. The limiting factor for the DOC efficiency is its light-off temperature, i.e. the temperature below which the oxidation is kinetically limited [5], which can reduce its efficiency, especially during urban operating conditions.

Other parameters also affecting the catalyst efficiency, apart from the temperature, are the exhaust gas residence time within the catalyst [6], the oxygen availability, the choice of catalytic components and loadings used to promote the oxidation reactions [7] and the ageing state of the coating and catalyst substrate caused by the thermal and chemical environment. Finally, the presence and concentrations of some exhaust species and their interactions with each other can also affect the catalyst behaviour, promoting or inhibiting oxidation, especially at low temperatures. Therefore, at an engine operating condition where the exhaust temperature is limited, pollutant removal could still take place, by encouraging promoting effects and limiting inhibition of DOC activity, which can be achieved with a clear understanding of these species interactions.

These interactions between exhaust components and their capacity to be oxidised have been researched and modelled using synthetic mixtures of gases to represent engine exhaust gas in order to understand the kinetics and oxidation mechanisms within the oxidation catalyst [7-13]. The majority of these studies focus on tracing the behaviour of an individual or a limited number of exhaust gas species in a synthetic gas mixture with a known composition. However, a single exhaust species can have different oxidation behaviour depending on whether it is studied on its own or as part of a mixture [13]. To our understanding the number of studies using actual engine exhaust gas to examine the interactions between different exhaust components is limited and focused upon exhaust gases from conventional fuel combustion [14-16]. In this study, a single cylinder engine is fuelled with diesel, alternative fuels and advanced combustion modes [17] to produce a variety of exhaust gases. The use

of genuine exhaust gas allows a valuable comparison with vehicle emissions met on the road and targeted by the emission legislations for air pollution. The efficiency of a DOC fed with these different exhaust gas compositions is studied in order to gain a wider knowledge of the diversity and priority among the various interactions existing between exhaust pollutant species (CO, hydrocarbon species and NO_x) within the DOC. A better understanding of these interactions and their effect (inhibition/promotion) on CO and HC oxidation can eventually support the design of the aftertreatment system to enhance the removal of pollutants, most especially at low temperatures.

Methodology and Experimental Setup

Methodology

In order to obtain a diverse spectrum of exhaust gas compositions, a single cylinder diesel engine was operated with different diesel fuels (diesel, Rapeseed Methyl Ester (RME), Gas-to-Liquid (GTL)) as well as with propane/diesel in a dual fuel combustion mode. Exhaust gas recirculation (EGR) was also used in most of the cases, as it is a well known engine calibration strategy currently used to reduce NO_x. During the experiment, the engine was run at a steady state point (40% load at 1500 rpm). In the case of the dual fuel combustion experiment, diesel was used as the pilot fuel and 0.2% or 0.5% of gaseous propane (based on the volume of intake air replacement) was injected in the intake manifold. These percentages were chosen in order to limit the usual loss in volumetric efficiency caused by the replacement of a portion of intake air by a gaseous fuel while maintaining combustion stability.

The concentrations of the engine exhaust species used to study the DOC activity are shown in Figure 1 a) and b) and were recorded under the following operating conditions:

- **Diesel without EGR** (Ultra Low Sulfur Diesel) used as a reference fuel produces the lowest level of CO and greatest level of NO.
- **Diesel with EGR** shows a significant reduction of NO_x emissions, while CO and THC concentrations are higher compared to diesel without EGR.
- **RME with EGR** produces a similar level of CO compared to diesel without EGR with a lower THC concentration. It is assumed that the exhaust content of aromatic hydrocarbons is lower (RME does not contain aromatics) than those emitted using conventional diesel but the hydrocarbons produced are on average heavier than for diesel [18,19].
- **GTL with EGR** produces a higher level of CO and a level of THC similar to the baseline. However, it is assumed that these hydrocarbons contain less aromatics than those emitted using conventional diesel, similarly to RME, as GTL does not contain aromatics. This condition also produces the lowest NO_x emission compared to the other studied exhaust gases.

- **Dual fuel combustion** shows a rather different exhaust gas composition compared to single fuel combustion, with a dramatic increase in CO and THC exhaust concentration. It also produces higher concentrations of light hydrocarbon species and especially light alkanes (propane) and alkenes (ethylene and propylene). Medium-heavy hydrocarbon concentration is similar to single fuel combustions, as those hydrocarbons are produced from the combustion of diesel fuel. The use of propane also produces a lower level of NO but increases the level of NO_2 compared to single fuel combustions.

For diesel fuel combustion, heavy hydrocarbons represent around 80% of the total hydrocarbon concentration found in the engine exhaust. Diesel/propane dual fuel combustion produces a more varied spectrum of hydrocarbon species as can be seen in Figure 1 b). Therefore, dual fuel combustion exhaust gases are used to study individual hydrocarbon species interactions while for the other fuels, only medium-heavy hydrocarbon oxidation is studied.

The exhaust system was fitted with a diesel oxidation catalyst and CO, HC species and NO_x conversion efficiencies were monitored during a heating temperature ramp. For every tests, the oxidation catalyst was subjected to a heating temperature ramp of around 2°C/min and an exhaust gas space velocity of 35,000/h. Engine out exhaust concentrations were measured at the beginning and at the end of each experiment in order to compare any changes in the exhaust gas composition during the test. Throughout the experiment, the evolution of the DOC outlet exhaust gas concentration was continuously recorded to calculate the conversion efficiency based on the inlet concentration.

The use of EGR in an engine decreases the oxygen content of the exhaust [20]. To eliminate the effect of this reduced oxygen availability on the catalyst activity, oxygen was injected upstream of the DOC when EGR was used, in order to maintain a similar level of oxygen at the inlet of the catalyst, for all the tests.

Experimental Setup

The engine used in this study is a single cylinder, direct injection, diesel engine [17]. The test rig is composed of a DC motor-generator dynamometer coupled to a load cell used to load and motor the engine. Other standard engine test rig instruments are used to monitor intake air flow, temperatures and pressures (air, oil, inlet manifold and exhaust system). The EGR system is externally cooled and its flow is controlled by a valve. The EGR level is determined volumetrically as the percentage reduction in volume flow rate of inlet air at a fixed engine operating point. The fuels used in the study were supplied by Shell Global Solutions UK and their properties can be found in [17].

A schematic of the experimental setup used in this study is shown in the Supporting Information section (Figure S1). A MultiGas 2030, FTIR spectrometry based analyser was used for the measurement of gaseous emissions (CO, HC and NO_x). A temperature controlled line was used to

direct a portion of the exhaust gas towards the catalyst placed in a furnace whose temperature was externally controlled. The sampling line temperature was maintained at 150°C to limit the condensation of hydrocarbons and water that could affect the measurements. The exhaust gas oxygen content was measured using an AVL DiGas analyser fitted with an electrochemical oxygen sensor. The measurement determined the quantity of oxygen to be added to the sample flow throughout the experiment, to equal the 15% oxygen concentration found in the engine exhaust gas when no EGR was used. The diesel oxidation catalyst used in this study is a 120 g/ft^3 Platinum/Palladium (weight ratio 1:1) with alumina and zeolite washcoat (2.6 g/in^3 loading) coated on a cordierite honeycomb monolith (25.4 mm x 91.4 mm) of 400 cells per in^2 and 4.3 mil wall thickness.

Results and Discussions

CO Oxidation

The start of CO oxidation in the DOC is dependent on its concentration in the exhaust gas (Figure 2). As CO concentration increases (except for diesel combustion without EGR), its light-off is delayed towards higher temperatures. CO can strongly adsorb onto active sites at low temperatures and cover the majority of the catalyst surface [7,8,14]. This, in return, limits oxygen access to the catalytic sites, preventing the start of CO oxidation which is directly released to the atmosphere. This CO self inhibition is reduced under lower concentration of CO, as can be seen in the case of RME exhaust gas.

The presence of hydrocarbons can also affect CO oxidation by competing for the same active sites. This inhibition can be altered as some of the hydrocarbons are adsorbed onto the zeolites coated on the catalyst, limiting the quantity of tailpipe hydrocarbons emitted at low temperature. The lower HC concentration recorded in the exhaust gas from RME combustion (Figure 1 a)) can also reduce the potential inhibition from CO and HC competition and allows earlier CO light-off. In dual fuel combustion, at 130°C-140°C, both CO and light alkenes (Figures 2 and 3) show some limited conversion (up to 15% conversion) which could highlight mutual inhibition as, similarly to CO, light alkenes strongly adsorb on active sites, due to their double bonds [9,21]. The greater light alkene concentration recorded in dual fuel combustion (Figure 1 b)) would therefore affect more CO light-off, as can be noticed in Figure 2. It is unlikely that propane has any influence on CO light-off as, when its oxidation starts, CO is already fully oxidised. Moreover, light alkanes adsorb poorly on metallic surfaces [11] and therefore are not supposed to compete to a large extent with respect to CO strong adsorption.

NO_x species can also compete with CO for adsorption and potentially inhibit CO oxidation [8,10]. It can be noticed that the exhaust gases containing the lowest NO concentrations are the ones showing an earlier CO light-off (RME, GTL and Diesel combustion with EGR). On the opposite, the exhaust gas from the combustion of Diesel without EGR contains the highest level of NO and the lowest level

of CO while showing a rather delayed start in CO oxidation. CO inhibition from NO is especially visible for diesel without EGR exhaust gas as CO presents some limited conversion between 50°C and 110°C (5% oxidation) before the reaction rate increases (Figure 2). This shows that even if CO oxidation starts at similar temperatures for diesel without EGR exhaust gas compared to the other exhaust gases, it remains limited to just a few percentage of conversion for some time before increasing again. The comparison of CO oxidation from diesel combustion with and without EGR confirms that a higher level of NO (diesel without EGR) seems to be more detrimental on CO light-off than a higher level of CO and HC (with zeolites present) for these ranges of concentrations. As can be noticed from the NO_x catalyst outlet concentration during the experiment (Figure 4), all exhaust gases show an increase of NO at low temperature from NO_2 partial reduction with hydrocarbons, except for diesel without EGR exhaust gas (NO remains constant before decreasing). It has been observed [14,22,23] that NO and NO_2 can easily adsorb onto Pt and Pd active sites and efficiently dissociate, producing a high coverage of adsorbed nitrogen species and oxygen atoms on the active sites and limiting other species adsorption (e.g. CO).

The competitive adsorption at low temperatures between CO, light alkene and NO_x species only happens once CO oxidation starts, as before that, CO was strongly covering most of the active sites. Once the temperature allows CO oxidation to start, its oxidation products desorb, freeing some active sites on which CO, as well as NO and alkenes try to adsorb [10]. This adsorption competition eventually reduces CO access to the active sites and limits its oxidation (5-10% conversion efficiency) over a certain range of temperatures until the other adsorbed species react and desorb, freeing the active sites for more CO to adsorb again, allowing the oxidation rate to increase.

While CO oxidation in the DOC is kinetically limited at low temperatures when exhaust gases from the combustion of RME, GTL and diesel with EGR are used, for the exhaust gas from the combustion of diesel without EGR and dual fuel combustion, the limiting factor is CO access to the active sites, as previously mentioned. Thus, once CO overcomes the inhibitions and adsorbs on the active sites at higher temperatures, its oxidation shows greater reaction rates as most of the catalytic sites were already kinetically active for CO oxidation. Another reason for the sharp increase in CO conversion efficiency noticed in dual fuel combustion exhaust gas is that CO oxidation reaction is exothermic. As CO concentration in dual fuel combustion is much higher than in the other exhaust gases, it involves a greater heat release during the reaction. This increases the catalyst local temperature once the oxidation starts and especially increases the catalytic site activity which would translate into greater reaction rate. As a result, the maximum CO conversion efficiency in dual fuel combustion is reached at similar temperatures to that of the exhaust gases from the other operating conditions, even though the light-off was considerably later.

Figure 5 summarises the required temperatures for the different exhaust gases to reach 10%, 50% and 100% CO conversion efficiency in the DOC. The graph shows that the exhaust gas with an early start of oxidation is not necessarily the one that will reach its maximum conversion first and that, after the oxidation has started, its reaction rate can still be affected by competition with other species. It can be noticed that the more the start of oxidation is delayed, the greater the reaction rate is.

Finally, once CO oxidation starts (Figure 2), some inflections can be noticed in RME and diesel combustion with EGR light-off curves at 120°C and 130°C respectively, as it has been noticed in other studies [10]. This change in oxidation rate can be related to an increase in medium-heavy hydrocarbon conversion happening at the same temperature (Figure 6). Once hydrocarbons are released from the zeolites and become active for oxidation, they compete for the same sites as CO, limiting its oxidation. This is particularly affecting RME as its hydrocarbon oxidation starts at lower temperatures and the hydrocarbons produced are on average heavier compared to other exhaust gases, possibly affecting CO accessibility to the active sites. Therefore, the competition for active sites takes place when the catalyst is not yet able to fully oxidise CO (only 55% conversion efficiency), affecting more strongly CO oxidation. This inflection in CO reaction rate can also be noticed for diesel with EGR. However, this effect is to a lower extent as hydrocarbons oxidise at higher temperatures (130°C), when more catalytic sites are available and active for both CO and HC oxidation, reducing the inhibition effect on CO. A minor slowdown in CO conversion can also be noticed at 135°C for diesel without EGR and 150°C for 0.2% propane, when hydrocarbon oxidation starts to increase. This effect cannot be noticed for the other exhaust gases due to either lower hydrocarbon concentration or hydrocarbon conversion starting at higher temperatures when a greater proportion of catalytic sites is already active for CO oxidation.

A schematic summarising exhaust species interactions affecting CO oxidation as presented above can be found as Figure S2 in the Supporting Information section of this paper.

HC Oxidation

Medium-Heavy Hydrocarbons

The oxidation catalyst used in this study contains zeolites which can trap medium-heavy hydrocarbons at low temperature and release them later on. Therefore, any low temperature conversion can be considered as 'virtual' conversion as the hydrocarbons are not actually oxidised but only removed from the exhaust gas and stored momentarily within the zeolites [24].

In Figure 6, it can be noticed that zeolites behave similarly for most of the exhaust gases used in the study, showing 60%-75% conversion efficiencies at 70°C. The light-off curve from the 0.5% propane dual fuel combustion behaves differently even though it contains a similar concentration of medium-heavy hydrocarbons. This highlights some strong inhibition effects as zeolite trapping efficiency is

reduced. A comparison between the exhaust composition from the combustion using 0.2% and 0.5% propane in the engine shows higher CO and light HC species concentration for 0.5% propane (Figure 1 b)). Nevertheless, these exhaust species would not have a direct deactivation effect on the zeolites activity as they are short hydrocarbon chains and therefore not trapped by zeolites. Further investigations are required in that case, in order to understand what would cause such a great inhibition in zeolites trapping.

Once the trapped hydrocarbons are released from the zeolites, different oxidation behaviours are recorded as the reaction activation energy and rate depend on the hydrocarbon nature, molecular structure (saturated, unsaturated, cyclic, aromatics, etc.) and chain length which influence their adsorption strength [12]. HC light-off curves from the combustion of RME and GTL show a plateau in conversion efficiency while hydrocarbon conversions from the rest of the studied fuels show a drop in conversion efficiency. This drop can be explained by the higher concentration of aromatic hydrocarbons in comparison to RME and GTL. Aromatic hydrocarbons require on average higher temperatures to get oxidised as they are more weakly adsorbed due to their ring shape and can suffer from inhibition from other species [13,21,25]. The depth of the loss in conversion efficiency depends on how efficiently these hydrocarbons are adsorbed on the zeolites and oxidised as they are released. The greater drop in conversion efficiency recorded is from dual fuel combustion exhaust gas which could be due to the presence of more numerous short chain hydrocarbons limiting the oxidation of the released hydrocarbons [9].

It has been previously reported that NO could compete with hydrocarbons for adsorption on the catalytic sites and limit their oxidation [8,26,27]. Nevertheless, several studies have also investigated the capacity of hydrocarbons to partially or completely reduce NO_2 to NO, depending on the type of hydrocarbon used [10,16,26,28]. Thus, the availability of NO_2 within the catalyst should be considered. It can be noticed on Figure 4 that no NO_2 is recorded at the catalyst outlet, even though NO_2 is present in the feed gas while the NO level increases. At low temperature, hydrocarbons are preferentially oxidised by NO_2. As the temperature increases, they start reacting preferably with molecular oxygen from O_2 rather than NO_2, which can be noticed by NO_2 concentration increasing again at the catalyst outlet and NO level reducing to its inlet value. However, it has to be pointed out that, based on the stoichiometric ratio required for hydrocarbon oxidation with NO_2, this reaction would account for only a limited oxidation of some hydrocarbons. This mechanism could explain the opposite behaviour of CO and HC light-off for diesel combustion with and without EGR, as diesel with EGR shows a greater drop in hydrocarbon conversion while having an early CO light-off compared to diesel without EGR. Therefore, the higher NO concentration which is detrimental for CO light-off could be promoting low temperature hydrocarbon oxidation through NO_2 production. NO and NO_2 can also be stored on the alumina washcoat and form nitrites or nitrates which hydrocarbons can react with [29,30]. This could also explain the improvement in the hydrocarbon conversion at low

temperature from diesel combustion without EGR and the lower NO concentration at the catalyst outlet.

CO has also been considered as an inhibitor for other species oxidation, as previously mentioned. From CO and HC light-off graphs (Figures 2 and 6), it seems that the start of hydrocarbon oxidation happens when a portion of CO had already been oxidised, around 50 % of the inlet CO, for most of the exhaust gases (Figure 7). Catalytic sites become available for hydrocarbons only after CO oxidation is already well developed [13]. As CO conversion efficiency increases, its concentration along the catalyst length decreases. This reduces CO inhibition effect on hydrocarbon oxidation by allowing them to adsorb on available catalytic sites at the rear of the catalyst brick. Therefore, before this threshold, as hydrocarbons are released from zeolites, most of the active sites can already be occupied by strongly adsorbed CO, covering the catalyst and limiting the ability of released hydrocarbons to adsorb on the catalytic sites.

Light Hydrocarbons

From propane, propylene and ethylene light-off curves, it can be observed that zeolites only selectively trap medium-long chain hydrocarbons at low temperature (Figure 6).

Propylene and ethylene oxidation starts at lower temperature than medium-heavy hydrocarbons and follows a steady increase until the maximum conversion efficiency, in a similar trend to CO light-off curve. Light alkene hydrocarbons are short chains of unsaturated hydrocarbons and therefore are more easily oxidised at lower temperatures than other hydrocarbons. Moreover, their oxidation does not suffer from competitive adsorption with other hydrocarbons but it can still be inhibited by a high light alkene concentration at low temperatures due to their strong adsorption onto the active sites [9,21], similar to CO. Light alkenes can also suffer from adsorption competition with CO at low temperatures, as previously mentioned, and it can be noticed that their oxidation commences only after CO oxidation has started, as more active sites become available for them to adsorb. The fact that they are less affected by competitive adsorption with other exhaust species justifies why the general trend of their light-off curve is not much altered when changing from 0.2% to 0.5% propane exhaust composition. The slightly delayed start of oxidation for 0.5% propane (around 20°C) can be justified by its higher alkene and CO content. Nevertheless, similarly to CO, once the oxidation starts, a greater reaction rate is recorded for 0.5% propane, leading to both dual fuel combustion exhaust gases reaching their maximum conversion efficiency at similar temperatures.

Propane, an alkane hydrocarbon, is a stable component due to its carbon atom being saturated by hydrogen, requiring more energy to be broken down and therefore greater temperatures to be oxidised. As previously mentioned, light alkanes are poorly adsorb on active sites and can be affected by the presence of other species. Therefore, their oxidation can only start when most of the other

exhaust components are already oxidised, especially strongly adsorbed CO and light alkenes. This is the reason why propane light-off and reaction rate are greatly affected by the change of exhaust composition and CO and hydrocarbon concentration increase from 0.2% to 0.5% propane.

Strategies to Enhance DOC Low Temperature Pollutant Removal

The above studied exhaust gas components and catalyst surface interactions allow the design of strategies to limit the quantity of pollutants emitted to the atmosphere at low exhaust temperatures. To promote low temperature CO oxidation, NO should be temporarily removed from the exhaust gas to reduce CO-NO_x adsorption competition. The use of EGR strategy also allows an improvement in CO light-off, by reducing NO engine out concentration, but care should be taken to limit possible fouling of the EGR cooler at low temperature (use of high pressure loop or temporarily by-pass the cooler at low temperature). Higher CO concentration can inhibit CO start of oxidation but can also increase its reaction rate once the reaction has started, due to the heat produced by exothermic CO oxidation. Moreover, trapping medium-heavy hydrocarbons through the use of zeolites can reduce the competition for active sites between hydrocarbons and CO, affecting CO oxidation rates (inflection in CO light-off curve) and delaying hydrocarbon start of oxidation. It is proposed in this study that promoting CO oxidation at lower temperature would allow more active sites to be available for adsorption, when hydrocarbons are released from the zeolites. In the meantime, hydrocarbons can react with stored NO_x and partially reduce them at low-medium temperatures. Light alkene hydrocarbons show early light-off and are not much affected by competition with other species apart from themselves and CO. Light alkanes on the contrary require higher temperatures to be oxidised. They do not affect other species oxidation but suffer from stronger adsorption of other species. Due to their short carbon chains, they are not efficiently trapped in zeolites and therefore are released into the atmosphere until the temperature is high enough to allow their oxidation. This study did not find any strategies directly promoting their oxidation, but lower temperature oxidation of other species (e.g. CO, light alkenes, etc.) can reduce competitive adsorption, increase active site availability and local temperature which can indirectly promote light alkanes oxidation.

This study gives tools to qualitatively predict how efficiently CO and different hydrocarbon species will be oxidised, based on the exhaust gas composition. It also gives an insight for the diesel exhaust aftertreatment design requirements, for selective momentary control of some species in order to promote the oxidation activity of the catalyst at low temperature. Thus, this study can generate ideas for identifying synergies between engines calibration (i.e. promotion of light alkenes during combustion instead of alkanes), fuels specifications and catalyst efficiency.

Acknowledgment

The University of Birmingham and Jaguar LandRover are acknowledged for the scholarship and sponsorship granted to Isaline Lefort. The authors would also like to thank Advantage West Midlands and the European Regional Development Fund, funders of the Science City Research Alliance Energy Efficiency project – a collaboration between the Universities of Birmingham and Warwick, for the equipment provided. Thank you also to Johnson Matthey for their technical support and to the Engineering and Physical Science Research Council (G038139) and TSB CREO project (400176/149) for their financial support.

Abbreviations

CO	Carbon Monoxide
CO_2	Carbon Dioxide
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
EGR	Exhaust Gas Recirculation
GTL	Gas to Liquid
HC	Hydrocarbons
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides
RME	Rapeseed Methyl Ester
SCR	Selective Catalytic Reduction
THC	Total Hydrocarbons

Supporting Information Available

Figure S1 is a schematic of the experimental set up used in this study. Figure S2 represents a schematic summary of the different interactions affecting CO oxidation. Before the oxidation starts, the catalyst is covered by carbonaceous species from CO, strongly adsorbed onto the active sites, restricting oxygen access and limiting CO oxidation. Later, once CO starts desorbing, other species adsorb onto the free active sites (first light alkenes and then nitrogen oxides) limiting CO adsorption and oxidation. Finally, when the oxidation is developing, medium-heavy hydrocarbons can also start

adsorbing on the active sites and compete with CO, affecting the reaction rate of CO oxidation (inflection in the light-off curve at higher temperatures). This information is available free of charge via the Internet at http://pubs.acs.org.

References

1. *Diesel Engine Exhaust Carcinogenic*, Press release n° 213, International Agency for Research on Cancer, 2012; http://www.iarc.fr/en/media-centre/pr/2012/pdfs/pr213_E.pdf.
2. Windeatt, J.; Brady, G.; Usher, P.; Li, H.; Hadavi, A. Real world cold start emissions from a diesel vehicle. *SAE Tech Paper Series* **2012**, 2012-01-1075; DOI 10.4271/2012-01-1075.
3. Schejbal, M.; Štěpánek, J.; Marek, M.; Kočí, P.; Kubíček, M. Modelling of soot oxidation by NO_2 in various types of diesel particulate filters. *Fuel* **2010**, *89* (9), 2365-2375; DOI 10.1016/j.fuel.2010.04.018.
4. Koebel, M.; Madia, G.; Elsener, M. Selective catalytic reduction of NO and NO_2 at low temperatures. *Catal. Today* **2002**, *73* (3-4), 239-247; DOI 10.1016/S0920-5861(02)00006-8.
5. Ye, S.; Yap, Y. H.; Kolaczkowski, S. T.; Robinson, K.; Lukyanov, D. Catalyst 'light-off' experiments on a diesel oxidation catalyst connected to a diesel engine—Methodology and techniques. *Chem. Eng. Res. Des.* **2012**, *90* (6), 834-845; DOI 10.1016/j.cherd.2011.10.003.
6. Madia, G.; Koebel, M.; Elsener, M.; Wokaun, A. The Effect of an oxidation precatalyst on the NO_x reduction by ammonia SCR. *Ind. Eng. Chem. Res.* **2002**, *41* (15), 3512-3517; DOI 10.1021/ie0200555.
7. Yao, Y-F Y. The oxidation of CO and hydrocarbons over noble metal catalysts. *J. Catal* **1984**, *87* (1), 152-162; DOI 10.1016/0021-9517(84)90178-7.
8. Voltz, S. E.; Morgan, C. R.; Liederman, D.; Jacob, S. M. Kinetic study of carbon monoxide and propylene oxidation on platinum catalysts. *Ind. Eng. Chem. Prod. Res. Develop.* **1973**, *12* (4), 294-301; DOI 10.1021/i360048a006.
9. Diehl, F.; Barbier Jr., J.; Duprez, D.; Guibard, I.; Mabilon, G. Catalytic oxidation of heavy hydrocarbons over Pt/Al_2O_3. Influence of the structure of the molecule on its reactivity. *Appl. Catal. B* **2010**, *95* (3-4), 217-227; DOI 10.1016/j.apcatb.2009.12.026.
10. Al-Harbi, M.; Hayes, R.; Votsmeier, M.; Epling, W. S. Competitive NO, CO and hydrocarbon oxidation reactions over a diesel oxidation catalyst. *Can. J. Chem. Eng.* **2012**, *90* (6), 1527-1538; DOI 10.1002/cjce.20659.
11. Yao, Y-F Y. Oxidation of Alkanes over Noble Metal Catalysts. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19* (3), 293-298; DOI 10.1021/i360075a003.
12. Mabilon, G.; Durand, D.; Courty, Ph. Inhibition of post-combustion catalysts by alkynes: a clue for understanding their behaviour under real exhaust conditions. *Stud. Surf. Sci. Catal.* **1995**, *96*, 775-788; DOI 10.1016/S0167-2991(06)81474-6.

400 13. Patterson, M. J.; Angove, D. E.; Cant, N. W. The effect of carbon monoxide on the oxidation
401 of four C_6 to C_8 hydrocarbons over platinum, palladium and rhodium. *Appl. Catal. B* **2000**, *26*
402 (1), 47-57; DOI 10.1016/S0926-3373(00)00110-7.
403 14. Watling, T. C.; Ahmadinejad, M.; Ţuţuianu, M.; Johansson, Å.; Paterson, M. A.J.
404 Development and validation of a Pt-Pd diesel oxidation catalyst model. *SAE Int. J. Engines*
405 **2012**, *5* (3), 1420-1442; DOI 10.4271/2012-01-1286.
406 15. Lafossas, F.; Matsuda, Y.; Mohammadi, A.; Morishima, A.; Inoue, M.; Kalogirou, M.;
407 Koltsakis, G.; Samaras, Z. Calibration and validation of a diesel oxidation catalyst model:
408 from synthetic gas testing to driving cycle applications. *SAE Int. J. Engines* **2011**, *4* (1), 1586-
409 1606; DOI 10.4271/2011-01-1244.
410 16. Katare, S.; Patterson, J.; Laing, P. Aged DOC is a Net Consumer of NO2: Analyses of
411 Vehicle, Engine-dynamometer and Reactor Data. *SAE Tech Paper Series* **2007**, 2007-01-
412 3984; DOI 10.4271/2007-01-3984.
413 17. Tira, H. S.; Herreros, J. M.; Tsolakis, A.; Wyszynski, M. L. Characteristics of LPG-diesel
414 dual fuelled engine operated with rapeseed methyl ester and gas-to-liquid diesel fuels. *Energy*
415 **2012**, *47* (1), 620-629; DOI 10.1016/j.energy.2012.09.046.
416 18. Ballesteros, R.; Hernández, J. J.; Lyons, L. L.; Cabañas, B.; Tapia, A. Speciation of the
417 semivolatile hydrocarbon engine emissions from sunflower biodiesel. *Fuel* **2008**, *87* (10-11),
418 1835-1843; DOI 10.1016/j.fuel.2007.10.030.
419 19. Ballesteros, R.; Hernández, J. J.; Lyons, L. L. An experimental study of the influence of
420 biofuel origin on particle-associated PAH emissions. *Atmos. Environ*. **2010**, *44* (7), 930-938;
421 DOI 10.1016/j.atmosenv.2009.11.042.
422 20. Ladommatos, N.; Abdelhalim, S. M.; Zhao, H. Effects of exhaust gas recirculation
423 temperature on diesel engine combustion and emissions. *Proc. Inst. Mech. Eng. J. Aut. Eng.*
424 **1998**, *212* (6), 479-500; DOI 10.1243/0954407981526127.
425 21. Mittendorfer, F.; Thomazeau, C.; Raybaud, P.; Toulhoat, H. Adsorption of Unsaturated
426 Hydrocarbons on Pd(111) and Pt(111): A DFT Study. *J. Phys. Chem. B* **2003**, *107* (44),
427 12287-12295; DOI 10.1021/jp035660f.
428 22. Parker, D. H.; Bartram, M. E.; Koel, B. E. Study of high coverages of atomic oxygen on the
429 Pt(111) surface. *Surf. Sci.* **1989**, *217* (3), 489-510; DOI 10.1016/0039-6028(89)90443-3.
430 23. Zheng, G.; Altman, E. I. The oxidation of Pd(111). *Surf. Sci.* **2000**, *462* (1-3), 151-168; DOI
431 10.1016/S0039-6028(00)00599-9.
432 24. Phillips, P.; Chandler, G.; Jollie, D.; Wilkins, A.; Twigg, M. Development of Advanced
433 Diesel Oxidation Catalysts. *SAE Technical Paper Series* **1999**, 1999-01-3075, DOI
434 10.4271/1999-01-3075.

435 25. Grbic, B.; Radic, N.; Terlecki-Baricevic, A. Kinetics of deep oxidation of *n*-hexane and
436 toluene over Pt/Al_2O_3 catalysts: Oxidation of mixture. *Appl. Catal. B* **2004**, *50* (3), 161-166;
437 DOI 10.1016/j.apcatb.2004.01.012.
438 26. Burch, R.; Millington, P. J. Selective reduction of nitrogen oxides by hydrocarbons under
439 lean-burn conditions using supported platinum group metal catalysts. *Catal. Today* **1995**, *26*
440 (20), 185-206; DOI 10.1016/0920-5861(95)00136-4.
441 27. Irani, K.; Epling, W. S.; Blint, R. Effect of hydrocarbon species on NO oxidation over diesel
442 oxidation catalysts. *Appl. Catal. B* **2009**, *92* (3-4), 422-428; DOI
443 10.1016/j.apcatb.2009.08.022.
444 28. Burch, R.; Breen, J. P.; Meunier, F. C. A review of the selective reduction of NO_x with
445 hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal
446 catalysts. *Appl. Catal. B* **2002**, *39* (4), 283-303; DOI 10.1016/S0926-3373(02)00118-2.
447 29. Oh, H.; Luo, J.; Epling, W. S. NO oxidation inhibition by hydrocarbons over a diesel
448 oxidation catalyst: reaction between surface nitrates and hydrocarbons. *Catal. Lett.* **2011**, *141*
449 (12), 1746-1751; DOI 10.1007/s10562-011-0714-z.
450 30. Burch, R.; Sullivan, J. A.; Watling, T. C. Mechanistic considerations for the reduction of NO_x
451 over Pt/Al_2O_3 and Al_2O_3 catalysts under lean-burn conditions. *Catal. Today* **1998**, *42* (1-2),
452 13-23; DOI 10.1016/S0920-5861(98)00072-8.

453 **Figure Caption**

454 **Figure 1:** Engine exhaust gas compositions (a) and exhaust hydrocarbon species concentration from
455 the engine operation on dual fuelling (0.2% and 0.5% propane with diesel) (b).

456 **Figure 2:** CO light-off curves from the different exhaust gas produced.

457 **Figure 3:** Light-off curves for light alkene (ethylene and propylene) and alkane (propane)
458 hydrocarbons for the dual fuel combustion mode.

459 **Figure 4:** NO and NO_2 catalyst outlet concentration over the temperature ramp (0°C representing
460 engine-out concentrations).

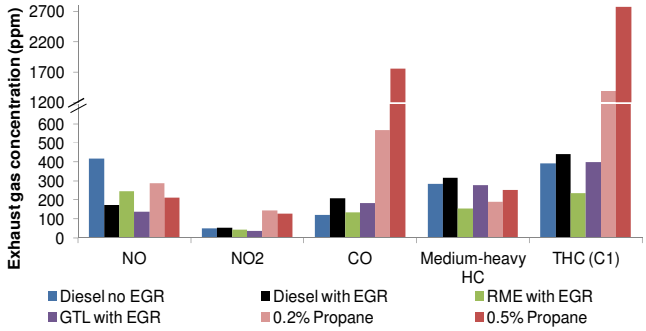
461 **Figure 5:** Catalyst inlet temperature required to reach 10%, 50% and 100% CO conversion for the
462 different tested fuels.

463 **Figure 6:** Medium-heavy hydrocarbon light-off curves.

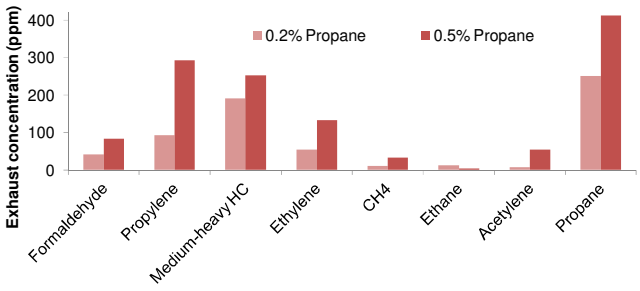
464 **Figure 7:** Catalyst inlet temperature required for 50% CO oxidation and for medium-heavy
465 hydrocarbon start of oxidation.

466

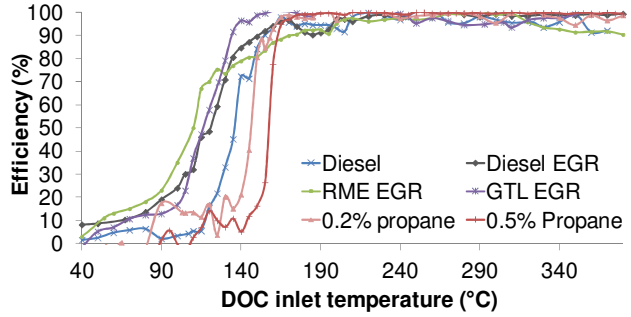
467



468

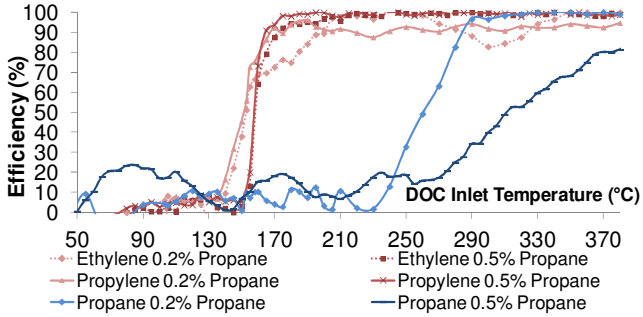


469 **Figure 1.**



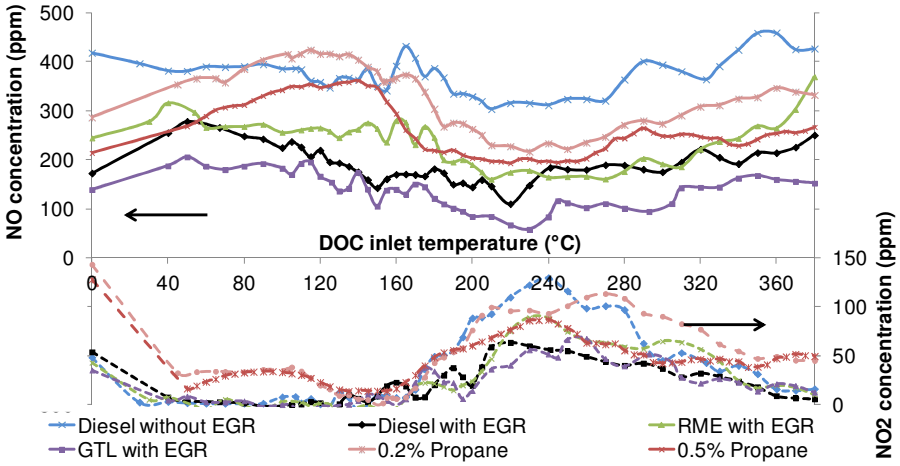
470

471 **Figure 2.**



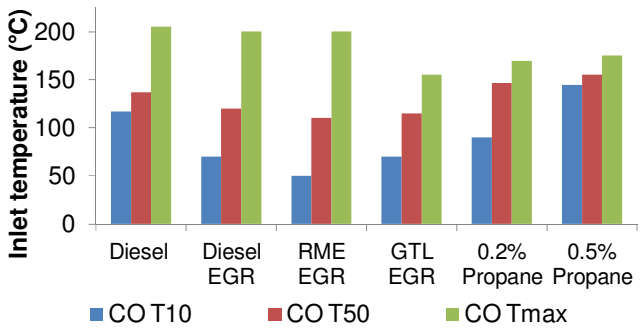
472

473 **Figure 3.**



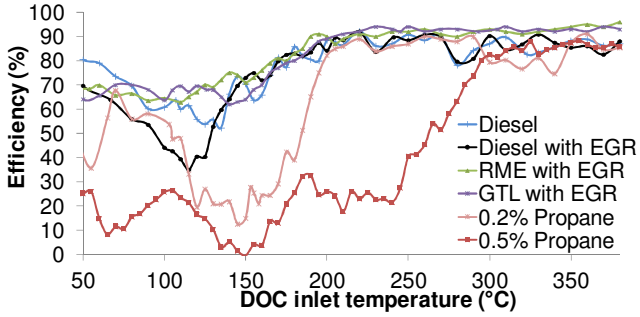
474

475 **Figure 4.**



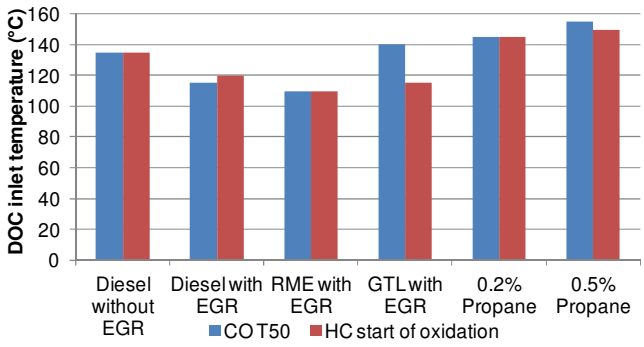
476

477 **Figure 5.**



478

479 **Figure 6.**



480

481 **Figure 7.**